

In-plane oxygens in high-temperature superconducting cuprates

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Abstract

The role of the oxygen degree of freedom in the cuprates' superconducting planes is analyzed in detail. Structural and photoemission results are reviewed to show that the most sparse description of the in-plane electronic states requires explicit control of the oxygens. For metallic states, the relative contributions of oxygen and copper vary along the Fermi surface (FS), with the arc metallicity dominantly oxygen-derived. For the magnetic responses, we find that the observed incommensurability arises naturally if one keeps separate the roles of the two sites. For the charge order in LBCO, we propose a scenario, based on magnetic interactions in the plane. We stress the need for further experimental investigations of the evolution of the intracell charge distribution with doping, and for a better theoretical understanding of the large particle-hole-symmetry breaking required for successful phenomenologies, but difficult to reconcile with ab initio calculations.

Key words: Emery model, magnetic fluctuations, electron-doped superconductors.

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1. INTRODUCTION

High-temperature superconductors have so far evaded attempts to reduce them to a simple model expression of the relevant physics. The physical reason for this is that they lie in a number of crossover regimes, between Mott antiferromagnetism (AF), different manifestations of metallicity, and superconductivity (SC), the precise nature of which is still a matter of considerable controversy. Simplicity usually corresponds to a limiting model situation, rather than to an interpolation between different limits, in particular the covalent and the ionic, as seems to be the case with the cuprates.

In the present work, we hope to convince the reader that the key simplifying step to a physical understanding of the cuprates is to take into account two physically distinct, and equally important, degrees of freedom in the copper-oxide planes, namely the coppers and the oxygens (Emery model). We find that further reduction to a one-band model is counterproductive, because it ends by reintroducing the particle-hole (*ph*) symmetry breaking, an essential feature of the experimental picture, in a physically less transparent way than if the oxygens were retained in the first place.

Investigating the relative role of oxygens and coppers in both the conductivity and SC presents a number of experimental opportunities, to distinguish the highest- T_c cuprates from cuprates with a lower T_c , or from similar materials, which are not superconducting. In our view, high- T_c SC cannot be reduced to its essentials in general, without first understanding what makes the concrete cuprates so special.

2. CRITICAL EXPERIMENTS

2.1. The LTT tilt

In the 214 class of high- T_c compounds, Ba-doped LCO and Nd-doped LSCO simultaneously develop a low-temperature tetragonal (LTT) phase, and a precipitous drop in T_c , around 1/8 hole doping [1, 2]. Thus the LTT tilt appears to be a critical probe into the high- T_c mechanism. It specifically affects the oxygens in the SC planes, splitting the degeneracy of O_x and O_y sites within a unit cell. A static intracell charge transfer is therefore expected to appear with the tilt, which may stabilize it, via the analogue of the Peierls mechanism [3].

The tilts are fairly small, about 3° , and have a large RMS scatter, nearly twice the mean

value [4]. While this observation led some to doubt [4] the coherent Peierls-like picture, it can only emphasize the critical sensitivity of the SC to a perturbation of the oxygen degeneracy. Significantly, the conductivity remains metallic, indeed with strong SC fluctuations above T_c around 1/8 doping [5]. Hence in this case SC does not vanish because an insulator has appeared, but because oxygen degeneracy is critical to SC coherence in high- T_c cuprates, for reasons remaining to be discovered.

2.2. Zinc substitution

The Zn-substitution effect is universal among the cuprates. The same 2–3% of Zn in place of Cu in the CuO_2 planes destroys SC at optimal doping both in hole-doped LSCO [6] and in electron-doped NCCO [7]. No structural change is involved, hence the effect is a local electronic probe into the SC mechanism. Zn is in the d^{10} configuration, precluding any hole occupancy on the Cu site, which reverts the neighboring oxygens back into the O^{2-} state of the parent insulator [8]. Both the Zn d -orbitals and O p -orbitals are closed, so the unit cell acts as a zero boundary condition for the holes on the CuO_2 lattice.

Significantly like the LTT tilt, Zn substitution does not destroy conductivity, albeit it introduces an finite upturn in the residual resistivity, similar to those uncovered by magnetic-field suppression. Changing the ionicity of the oxygens by Zn amounts to a strong perturbation of the relative oxygen site energy, pointing, again, to the critical importance of site order on the oxygens for the SC, as distinct from the conductivity, in the cuprates.

Zinc most effectively destroys SC in underdoped YBCO and low- T_c compounds, which only show a Fermi arc in ARPES. In optimally doped YBCO, and, importantly, overdoped compositions, where the FS is well developed even if T_c is not the highest, it is much less effective [9]. By topological arguments within the Emery model, the wave-functions near the vH singularities are copper-dominated, while, as we shall see below, the Fermi arcs are oxygen-dominated in the parameter regimes required for a successful phenomenology. Hence it would appear that the oxygens are primary in the SC pairing, while the coppers play a supporting role, most simply imagined as a density-of-states effect, although other scenarios, involving the mechanism of the SC pairing around the antinodal point more directly, are also possible.

Nickel is markedly less effective than Zn in destroying SC [10]. The open d -orbitals in Ni

may hybridize with the oxygens, so the latter remain in the covalent limit. We thus expect Ni substitution to suppress T_c less efficiently in underdoped cuprates on the hole side, and in all cuprates on the electron side, because it affects the oxygens less, which we regard as primarily responsible for the SC in those compounds. In optimally hole-doped or overdoped cuprates, its effects should increase with the role of Cu sites in SC.

3. COVALENCY IN THE THREE-BAND PICTURE

3.1. Hopping overlaps

It has long been recognized that the three-band model has to be applied to ARPES in the cuprates in a physical regime, different than the one inferred from quantum-chemical calculations [11]. The latter would have a Cu–O overlap $t_{pd} \gg t_{pp}$, the O_x – O_y overlap, which however results in a FS, rotated by 45° with respect to experiment. It was noticed very early [12] that the large on-site repulsion U_d on the coppers effectively reduces the value of t_{pd} . However, that effect cannot explain the dominance of t_{pp} in ARPES.

First, the physical regime predicted by *ab initio* approaches is borne out by high-energy XPS measurements [13]: XPS and ARPES really observe different high- and low-energy physical regimes, respectively. More revealingly, to fit ARPES, it is not sufficient to decrease t_{pd} : one must have a t_{pp} absolutely larger than any *ab initio* calculation to date has justified. The measured dispersion of the open band in the $(0,0)$ – (π,π) (diagonal) direction is about 0.8 eV wider below the Fermi level (i.e. ~ 1.5 eV overall) than can be justified *ab initio* [14]. Adding magnetic correlations is expected to decrease t_{pp} , hence the discrepancy is not merely large, but goes the wrong way, as well. Because t_{pp} is uniquely dispersive in the diagonal direction, by topology of the lattice alone, copper-based correlation effects are poor candidates to explain the absolute scales of the open bands in BSCCO and YBCO, although they can depress the ratio $|t_{pd}/t_{pp}|$.

Finally, there is no indication of a t_{pd} -driven paramagnetic band-width collapse near the metal-insulator transition, as expected in the mean-field framework [15]. Chemical potential data are consistent with the picture that the first doped holes already occupy a hybridized band [16]. Simply, coherent hopping remains possible even in the presence of a large (dynamic) charge and spin disorder on the coppers, indicating, again, the importance

of t_{pp} . The insulating state at small dopings is reached in this picture via superexchange, which orders the coppers at the expense of the residual oxygen conductivity.

3.2. Site energies

The site energies show a similar discrepancy between high-energy (XPS) and low-energy (ARPES) experiments. While XPS confirms the LDA prediction of a large charge-transfer gap Δ_{pd} , i.e. $U_d > \Delta_{pd} > |t_{pd}| > |t_{pp}|$, ARPES fits require quite a different regime, $4|t_{pp}| \gtrsim \Delta_{pd} > t_{pd}^2/\Delta_{pd}$. Clearly the band parameters must be strongly renormalized to pass from one to the other. The physical distinction of the latter is that it brings the bonding “copper” band in anti-crossing with the next, “oxygen” band (non-bonding at $t_{pp} = 0$), such that the Fermi arcs of the hybridized open band are in fact oxygen-like. This is most striking in NCCO [17]. The metal-insulator transition itself has been proposed to proceed by delocalization of oxygen holes following an $O^{2-} \rightarrow O^{1-}$ orbital transition [8]. The low-energy regime, seen in ARPES, is the normal state precursor to SC. It is in this low-energy regime that SC is critically sensitive to perturbations of the oxygen sites, as discussed above.

It is still an open question, to what extent the regime, in which the (renormalized) copper and oxygen states anticross close to the Fermi level, is common to the cuprates. The rapid evolution of the FS with doping in LSCO suggests, assuming the Hartree-Fock (HF) picture, a similar evolution of the Cu vs. O charge content in the SC compositions. On the other hand, a notable EELS experiment [18] indicates nearly complete oxygen dominance of the conducting bands in both LSCO and YBCO, while the latter shows little FS evolution with doping. Evidently the site content in the conducting states may not be directly inferred from the HF three-band model fits. A more sophisticated accounting is currently under way, based on the idea [19], that a significant redistribution of copper spectral strength into localized states is possible when the Hubbard $U_d \rightarrow \infty$, because the charge-transfer scale then appears as the dominant “slow” counterpart to the “fast” interference of the empty upper and filled lower Hubbard band, the latter pushed to infinity at infinite U_d , with finite spectral weight. The mechanism by which this occurs is a kinematic waiting effect, namely an itinerant hole cannot hop on the copper site if another is already there, but has to wait for the other to depart. This waiting also gives rise to an effective scattering $U_{d\mu} \sim t_{pd}^4/\Delta_{d\mu}^3$ between itinerant states on oxygens, where, critically, $\Delta_{d\mu}$ is the difference between the

energy of the d^9 copper site level and the chemical potential, not the oxygen level as in the usual expression for superexchange. Hence a magnetic scale appears near optimal doping, where superexchange effects are presumably small, by virtue of the oxygen metallicity.

3.3. Relation to the one-band model

To fit experiment, additional hopping terms are usually added to the t - J model, the first of which, t' , breaks ph symmetry, as does the t_{pp} term in the three-band model. Often even further terms are introduced, turning the model dispersion into an effective Fourier-Taylor series, which can easily fit any observed FS [20]. However, when ph -symmetry-breaking terms are properly disentangled [21] from the symmetry-preserving ones, it turns out the correction outweighs the initial term by a factor of 3–8 in realistic fits, because the relevant ratio is $|4t'/(t + 2t')|$, with $t'/t < 0$, not $\sim |t'/t|$, as one might naively assume.

Such dominance of the correction means that the mapping of the three-band onto the one-band dispersion is singular in the physical regime actually observed in the cuprates, as also indicated by unrealistically long-distance hopping terms, amounting to a diverging Taylor series. Reduction to the one-band dispersion thus involves considerable difficulty in establishing the physical meaning of comparisons with experiment, and in addition control over the relative spectral weight of Cu and O sites is lost. Retaining both coppers and oxygens explicitly is in our view the appropriate simplification, allowing for their different physical roles.

4. MAGNETIC RESPONSES

Magnetic response in the SC cuprates is generally incommensurate [22–24]. We have previously connected the peak-rotation and “arc-protection” effects [25]. Here we present a simple qualitative mechanism, by which the complexity of the cuprates can give rise to an incommensurate magnetic response already at low order, one-loop level.

First, the magnetic interactions of the hybridized extended states are mediated by scattering on the coppers, hence the vertices of the ph bubble involve the corresponding projectors. Because the two legs of the bubble are at different k -vectors, convoluting them can give a minimum at the commensurate (π, π) point, if t_{pp} is strong enough. The second effect is

the known weakening of the log-squared SDW response at the vH filling to log when ph symmetry is broken [26], e.g.: $\ln^2 \omega \rightarrow \ln |2t'/t| \ln \omega$ in the one-band model. Again, if t_{pp} is large enough, the prefactor can weaken the logarithm quantitatively, as in $\ln 1 \approx 0$. Finally, the logarithm is sensitive to disorder: even a 1 K broadening in the single-particle lines is enough to suppress it below the incommensurate peaks surrounding the minimum created by the projectors. The situation is summarized in Fig. 1 for the vH filling itself, noting that realistic SC compounds have an open large Fermi surface, hole-doped relative to it.

All three effects are due to copper-oxygen complexity. Site projectors are relevant in multiband situations, especially if the interaction is localized in real space. The weakening of the logarithm is due to ph symmetry breaking, not present in simplified models like t - J . The qualitative effect of weak disorder is only expected to be universal in materials sufficiently complex, for a small broadening to be an intrinsic property. The ensuing incommensurate AF is in the strong-coupling limit, because the side peaks are finite, so a transition can be obtained in magnetic mean field only for a finitely strong spin-flip coupling vertex.

5. CHARGE AND SPIN ORDER IN LBCO

In the LTT phase of LBCO, both charge (CO) and spin (SO) collinear stripe order have been observed in the depression of SC near the $1/8$ anomaly [27]. The wavelengths are very short, $\mathbf{q}_{CO} = 0.54\pi/a$ for $x = 1/8$, and connected by the interesting relation $\mathbf{q}_{CO} = 2(\mathbf{q}_{SO} - \mathbf{Q}_{AF})$. The transition temperatures are always arranged $T_{LTT} \geq T_{CO} > T_{SO}$, with $T_{LTT} = T_{CO}$ for $x < 1/8$. The coupling of SO to CO via a third-order “S²C” invariant was proposed previously [28], which accounts for the factor of 2 in the wave-vectors. The principal remaining question is whether the driving mechanism comes from CO or SO.

At fillings $x > 1/8$, T_{CO} is markedly less than T_{LTT} , and \mathbf{q}_{CO} appears as in a second-order transition, while LTT is first-order. For $x \approx 1/8$, the two temperatures coincide, while for $x < 1/8$ we concur [27] that the apparent coupling, $T_{LTT} = T_{CO}$ for $x < 1/8$, is most probably a background effect: the observed CO can only exist in the LTT phase. The steady lowering of T_{CO} below T_{LTT} for $x > 1/8$ is naturally understood if the two transitions are not due to a divergence of the same susceptibility, i.e. the driving mechanisms are different.

A tentative complete scenario rests on the observation [27] of long-, but not infinite-range SDW correlations, for $T_{SO} < T < T_{CO}$, hence T_{CO} behaves as T_{MF} (mean-field) for SO.

Coulomb interactions are 3D, while magnetic interactions are 2D, mediated by covalency. We propose it is really SO which is driving CO via the “S²C” invariant, only CO can get stabilized already at the higher T_{MF} , because it is helped by the 3D nature of the Coulomb forces, while the covalency between planes is negligible by comparison. This scenario is corroborated by the fact [27] that CO melts in all three directions simultaneously. It is also conventional to expect that short-range Coulomb interactions can contribute to the distinction between the LTT and LTO backgrounds, although the precise manner remains to be determined. Conversely, for a phonon to be responsible, a mode would have to exist, of which we are not aware, with significantly different dynamics in the two phases.

6. DISCUSSION

The metallization of the cuprates against a strong ionic background has been a persistent challenge both to theory and interpretation of particular experiments. Our picture is broadly based on the crossover, at extremely small dopings, between the AF-assisted Mott-localized state and the state, which is a mixture of coherent extended, and incoherent single-particle states, localized within a CuO₂ unit cell. The extended states are O-dominated, while the localized ones are Cu-based. Their localization is due to incoherent Cu–O charge transfer excitations within the CuO₂ unit cell, analogous to the mixed-valence fluctuations in heavy-fermion systems. On the other hand, the discommensuration of magnetic correlations is associated with spin-flip excitations between extended states. Recent NMR investigations have directly been interpreted in terms of a two-component picture [29]. Similarly, observations of a T^2 dependence of the conductivity in the pseudogap state indicate a Fermi-liquid-like metallic component [30], which we believe is oxygen-based.

Direct O–O hopping changes the AF at the vH filling from commensurate to incommensurate. Its effect on the metallic band is even more dramatic, as the *ab initio* approaches, which start from a copper d⁹ state, are unable to account for a large part of the dispersion in the Γ – M direction. This may be related to a long-predicted orbital transition with doping [8], from Cu²⁺–O^{2−} to Cu¹⁺–O^{1−}, which gives a plausible microscopic interpretation of the oxygen-dominated anticrossing regime, to which we were independently led by ARPES in NCCO, although, to repeat, reproducing ARPES requires a large t_{pp} in all cuprates.

A two-component picture is indicated for SC as well, although it is too early to pronounce

definitively on the relative roles of Cu and O sites. SC seems first to appear on the oxygens, although it is more robust where coppers are also involved at the Fermi level. We trust the simple and transparent two-component picture, based on the physical lattice states, to play an important role in the eventual understanding of the high- T_c cuprates. We suggest further experimental effort, in particular with local probes, to be directed at disentangling the roles of the two sites.

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Figure 1. The static bare susceptibility $\chi_0^\pm(\omega = 0)$. Thin, thick, and dashed lines indicate no damping, 1 K, and 10 K damping, respectively. Note the broad minimum of the background at M (π, π) , due to O–O hopping in the anticrossing regime. The collinear maxima determine the magnetic incommensurability.

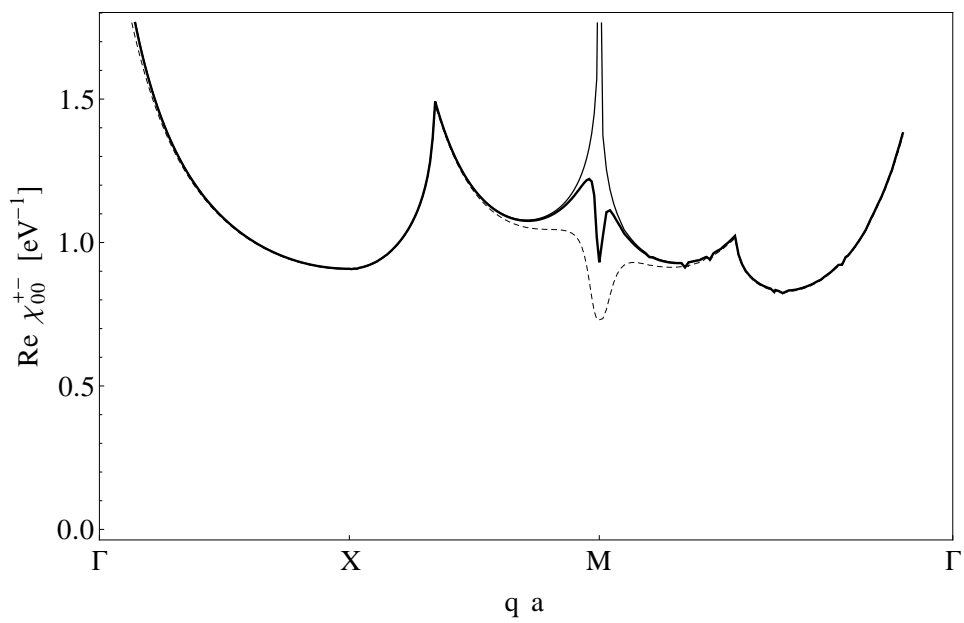


Figure 1.